A STUDY OF SOME REACTIONS
OF
METALLIC OXIDES, FATTY ACIDS
AND THE GLYCERIDES OF FATTY ACIDS.

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WAYLAND B. LIVERMORE S.B.

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A STUDY OF SOME REACTIONS OF METALLIC OXIDES, FATTY ACIDS AND THE GLYCERIDES OF FATTY ACIDS.

INTRODUCTION.

This research was undertaken with the purpose of studying the reactions between metallic glycerides and fatty acids, and between metallic oxides and the glycerides of fatty acids.

These reactions, especially the former, are of some importance and interest in the paint industry. Litharge, and the oxides of some other heavy metals, are cooked into linseed oil in the manufacture of boiled oils and in the preparation of driers for use in making varnishes. However, little study seems to have been made of the actual reactions involved in this process. Chemical literature gives practically no information on the subject, other than to state that a metallic linoleate is the product of the reaction. No mention is ever made of what happens to the glycerine which is replaced by the litharge.

If the reaction is a simple replacement, it should be possible to cook in only one and one-half moles of litharge per mole of linseed oil. The reaction would take place according to the equation

$$2\,C_3H_5(RCOO)_3 + 3\,PbO + 3\,H_2O \longrightarrow 2\,C_3H_5(OH)_3 + 3(RCOO)_2Pb,$$

where R may represent any of the several fatty acid radicals of linseed oil. However, Stoppel[1], Technical Director of Valentine and Company, states that it is actually possible to cook in two moles of litharge and keep that quantity in solution. He also says that a third mole may be cooked in, but, in so doing, a white or gray crystalline precipitate is formed.

Stoppel has suggested a theory to account for these facts. He thinks that when two molecules of litharge react with one molecule of linseed oil, one litharge molecule replaces two fatty acid radicals of the linseed oil molecule, while the other molecule of litharge reacts with the liberated fatty acid to form a molecule of lead linoleate.

Stoppel has done some work toward proving this theory. He found that the molecule, which he supposed to contain one lead atom and one fatty acid radical combined with a glyceryl group, was less soluble in certain paint thinners than the normal lead linoleate. He thus separated it by fractional crystallization and found its ash content to agree with that called for by theory.

He was also able to synthesize the same compound by first heating glycerine with litharge, whereby the lead glyceride having the formula $C_3H_5(OH)O_2Pb$ was formed. He then dissolved this in the theoretical quantity of the fatty acids from linseed oil. He found this compound to have properties identical with those of the compound prepared by the action of litharge on linseed oil.

This piece of research was undertaken with the purpose of

[1]Personal communication.

further studying these types of reactions, in order to obtain more evidence either for or against this theory. In view of the relative complexity of the linseed oil molecule, it was decided to use an analogous substance having a simpler and more definite composition. The reactions would evidently be the same, and the work would be somewhat simplified. Stearin was selected as being a simple triglyceride containing but a single fatty acid. It was thought at the time that the substance would be readily available. That such is far from true was discovered later.

The work necessary to the study of these reactions divided itself into three parts. First: to prepare the lead glyceride by heating glycerine with litharge. Second: to react this compound with stearic acid and determine in what manner the reaction takes place. Third: to determine whether or not the same product is formed when litharge is heated directly with stearin. In both the second and third reactions apparently a compound should be formed where glycerine acts as the base and both litharge and stearic acid act as the acid. Lead stearate should also be formed in the third reaction and possibly in the second.

PROCEDURE AND RESULTS.

Preparation of Lead Glyceride.

The first step in the research was the preparation of the lead salt of glycerine, by the action of litharge on glycerine. This reaction takes place according to the equation

No attempt was made to determine which two hydroxyl groups would be replaced by the lead atom, since this fact would be immaterial in the ultimate analysis of the compound. It was only necessary to know that one molecule of litharge reacted with one molecule of glycerine. The structural formula for the lead glyceride is written as above only for the sake of symmetry. The above reaction is used in the preparation of a litharge-glycerine cement, as described by Mervin[2].

An attempt was made to prepare anhydrous glycerine for use in the reaction, since the lead glyceride is rather easily decomposed by moisture, especially at boiling temperatures. Ordinary glycerine was heated in a distilling flask connected to a condenser, appropriate receiver, manometer and filter pump. The glycerine was kept at a temperature of 90°C., under a pressure of 12 mm. of mercury, for a period of six hours. Water distilled off and the glycerine decomposed slightly, as evidenced by an acrid odor in the distillate and a darkening of the glycerine. The glycerine could not be further purified by distillation, due to the fact that it decomposed considerably at its boiling point, even at low pressures. Anhydrous copper sulfate could not be used as a final dehydrating agent, due to a slight solubility of the salt in the glycerine.

The glycerine treated in the above manner did not seem to give any appreciably better reaction with litharge than ordinary 90%

[2]Jour. Ind. Eng. Chem., 9, 390.

glycerine. The reaction took place satisfactorily using ordinary glycerine, without apparent decomposition of the product. Therefore it was decided to use ordinary glycerine, rather than to attempt the somewhat laborious task of obtaining it in an anhydrous condition.

In the following reaction litharge was combined with four times the theoretical amount of glycerine. 60 c.c. of glycerine were heated in a beaker to a temperature of 90°- 100°C., using a water bath to maintain the temperature at this point during the reaction. 42 grams of litharge were added gradually during a period of one hour. The reaction mixture was agitated continuosly with a mechanical stirrer to prevent cement formation. The orange color of the litharge gradually disappeared as the reaction progressed. After six hours the reaction seemed to be as complete as possible. The mixture was nearly white, although a considerable amount of litharge had settled to the bottom without reacting.

The reaction mixture was agitated with anhydrous alcohol to remove unconverted litharge. After several decantations the suspension of lead glyceride in alcohol was filtered with the aid of suction. The product was treated with another portion of alcohol and vigorously agitated to break up the larger aggregates of particles. After two such treatments the compound was obtained in what appeared to be a pure state. The product was seperated by filtration, dried in a desicattor, and then heated in an oven for one hour at 100°C.

The lead glyceride was very slightly soluble in alcohol, or ether, and insoluble in benzene. It decomposed rather readily in the presence of water, especially when heated to boiling. On boiling with water it hydrolyzed with the formation of a yellow precipitate, presumably litharge. The compound decomposed more readily in the presence of

acids, forming glycerine and the lead salts of the acids. It decomposed without melting when heated. When ashed, the residue was partially lead and partially lead oxide.

The compound was analyzed to determine the percentage of lead that it contained. One gram samples, previously dried for an hour at 130°- 140°C., were treated with 50 c.c. of water and 2 c.c. of dilute acetic acid. The mixture was boiled until hydrolysis was complete, and the lead precipitated as lead oxalate, by adding an excess of oxalic acid (25 c.c. of a 5 % solution). The precipitated lead oxalate was filtered on weighed Gooch crucibles, washed with 200 c.c. of water, then with a little 50 % alcohol, and dried in an oven for two hours at 130°-140°C.

The lead was determined as the oxalate rather than as the sulfate due to the fact that the presence of glycerine in the solution, from the hydrolysis of the lead glyceride, might have resulted in carbon formation in the presence of concentrated sulfuric acid. Lead oxalate is a salt more insoluble than lead sulfate and stable under the conditions of the experiment.

The results of the analysis were as follows:

	I	II
Weight of sample analyzed	1.2680 gms.	1.1547 gms.
Weight of lead oxalate precipitate	1.2462 gms.	1.1345 gms.
Percentage of lead (found)	69.00 %	68.98 %
Percentage of lead (theoretical)	69.71 %	69.71 %
Average percentage of lead found		68.99 %

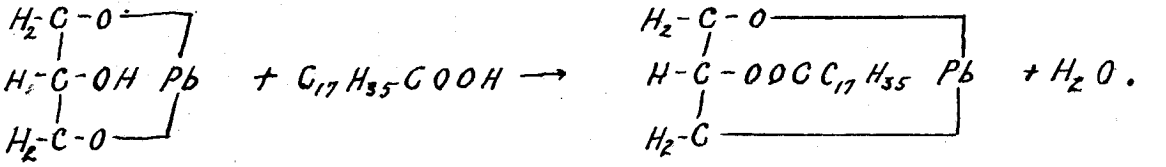
The reaction had evidently taken place as expected and the compound was considered to be sufficently pure for use in the next reaction.

Reaction of Stearic Acid and Lead Glyceride.

The second step in the research was the combination of the lead glyceride with stearic acid. The stearic acid used had previously been crystallized from alcohol. It had a melting point of 60°C., which was not changed by recrystallization from alcohol and from ether.

The lead glyceride was found to be quite readily soluble in stearic acid at a temperature of 80°- 100°C. As might be expected, it dissolved more readily if an excess of stearic acid was present. The reaction mixture, when the excess had been extracted with ether, yielded a new substance insoluble in the ether.

According to the theory already given, the reaction between the two compounds should take place as shown by the equation



Therefore an attempt was made to dissolve the lead glyceride in an equimolar amount of stearic acid. To two grams of stearic acid, at a temperature of 80°C., was added the theoretical amount, 2.08 grams, of lead glyceride. The solid did not dissolve completely, even after four hours of heating at the above temperature. Some solution did take place, but there was a considerable amount of undissolved residue.

It was thought that the reaction would take place in the same way and with greater facility, if an excess of stearic acid was used. Accordingly, an experiment was tried, similar to the above, but using five times the theoretical amount of stearic acid. Solution was complete

after heating the mixture for four hours in a crucible, in an oil bath, at 80°C.

The reaction mixture was cooled, pulverized, and treated with 100 c.c. of dry ether to remove excess stearic acid. The mixture was refluxed for one-half hour and then filtered. The product, without further purification, was examined superficially to determine its properties. The substance was insoluble in alcohol and ether. It was not appreciably hydrolyzed by cold water, but hydrolyzed when boiled with water for some time. The presence of acids or alkalies increased the rate of hydrolysis considerably. The products of hydrolysis were stearic acid, glycerine, and a lead salt. An oily layer was formed on the surface of the water during hydrolysis.

Since the reaction seemed to take place in a satisfactory manner under the above conditions, it was carried out using larger quantities. 25 grams of stearic acid were heated in a crucible, in an oil bath, to a temperature of 80°C. The acid was stirred with a mechanical stirrer and 5.2 grams of lead glyceride were gradually added during a period of one hour. The mixture was kept at the above temperature for four hours, at the end of which time solution was complete. The whole time of reaction was nearly five hours. The temperature was purposely kept as low as possible to avoid undue decomposition of the acid. Even at the temperature used, some decomposition did take place, as evidenced by a slight darkening of the mixture.

The reaction mixture was pulverized and refluxed for one hour with 500 c.c. of dry ether, to insure complete removal of excess stearic acid. It was then filtered, washed well with ether on the filter paper, and dried in an oven for an hour at 50°C. From the ether solutions used

in the purification process about 20 grams of stearic acid were recovered. Although no attempt was made to determine this amount accurately, nevertheless it seemed to indicate that the lead glyceride had combined with about the theoretical amount of the acid.

The purified product was not appreciably soluble in most solvents. It was only very slightly soluble in alcohol, ether and benzene in the cold. It dissolved partially in hot benzene and formed a clear solution in hot turpentine. This was the only solvent used which dissolved the substance completely. An attempt was made to further purify the substance by recrystallization from hot turpentine, but this was unsuccessful. The substance which serarated as the turpentine cooled did not resemble the original substance physically. It was a rather gummy mass without apparent crystalline form.

The substance was not wetted by water, but was fairly easily hydrolyzed by hot water. In the presence of acids or alkalies the hydrolysis was much more rapid. Hydrolysis produced an oily layer on the surface of the water, which solidified at about 60°C. It was probably stearic acid. When acetic acid was used in the hydrolysis, the oily layer was found to contain traces of lead; whereas, if a steng acid was used, no traces of lead were present in this layer. If the lead was removed from the water solution, by precipitation as lead sulfate, and the filtrate from this precipitation was evaporated to dryness, the presence of organic matter was indicated by carbon formation and by an acrid odor. The substance seemed to hydrolyze to stearic acid, glycerine and a lead salt. The substance had a melting point of 111°- 112°C., this melting point not being very sharp.

In order to determine the probable composition of the reaction

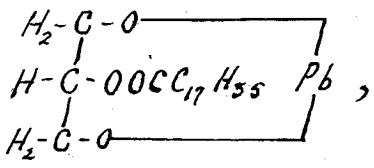
product, one and one-half gram samples were analyzed for lead in the following manner. The samples, previously dried and weighed, were ashed in small casseroles to remove organic matter. The residues, mixtures of lead and lead oxide, were dissolved in 10 c.c. of concentrated nitric acid and the solutions evaporated to dryness to remove excess nitric acid. The lead nitrate residues were dissolved in 50 c.c. of water and the lead precipitated as the oxalate by adding an excess of oxalic acid (20 c.c. of a 5 % solution). The precipitates were coagulated by digesting them for a short time at 90°C., and then filtered on weighed Gooch crucibles. The precipitates were washed with 200 c.c. of water and then with a little 50 % alcohol, and dried in an oven for an hour at 130°-140°C.

The above method of analysis was the one used in all following cases for the determination of lead.

The results of the analysis were as follows:

	I	II
Weight of sample analyzed----------	1.6317 gms.	1.5497 gms.
Weight of lead oxalate precipitate-----	0.6272 gms.	0.5953 gms.
Percentage of lead found----------	26.98 %	27.14 %
A verage percentage of lead found----------		27.06 %

If the substance had consisted wholly of the compound B-stearo-lead glyceride, having the formula



it should contain 36.77 % lead. Since it seemed unlikely that impurities in the substance of errors in the experiment could have produced so large

a deviation, it was thought probable that the reaction had produced either some other compound, or a mixture of two or more compounds.

In order to make more certain that the substance was as pure as possible, it was further treated with dry ether, refluxed as before, and filtered and dried. Another analysis made on this product gave the following results:

	I	II
Weight of sample analyzed----------	0.6487 gms	0.9185 gms.
Weight of lead oxalate precipitate----	0.2604 gms.	0.3618 gms.
Percentage of lead found----------	28.13 %	27.65 %
Average percentage of lead found----------		27.89 %

Since it seemed somewhat probable that the substance was a mixture of two or more different compounds, an attempt was made to separate these components. The substance was treated with hot benzene, whereby a portion of it dissolved. The undissolved residue was filtered off and extracted a second time with hot benzene. It was somewhat whiter in color than the original mixture, and had a more definite melting point, 109.5°- 110°C.

The benzene solution, on cooling, deposited an amount of white solid roughly equal in volume to the amount dissolved by the benzene. This substance might have been lead stearate, as this compound is soluble in hot benzene, but insoluble in cold benzene.

A further study of these two components was impossible due to the fact that only a small quantity of each remained after the separation had been made. However, from the tests made, it was indicated that the reaction product was a mixture containing at least two different substances. It could have been a binary mixture of lead steatate and B-stearo-lead

glyceride, since the percentage of lead found agrees with a possible mixture of these two components. The reaction had not proceeded as expected for some reason or other.

In order to determine more favorable conditions for the stearic acid-lead glycerine reaction, the reaction was tried using different proportions of the two reactants, as follows:

No. 1----- 1 mole of lead glyceride and $\frac{1}{2}$ mole of stearic acid.

No. 2----- 1 " " " " " 1 " " " " .

No. 3----- 1 " " " " " 2 " " " " .

No. 4----- 1 " " " " " 3 " " " " .

The reactions were carried out by intimately mixing one-half gram of lead glyceride with the corresponding amount of stearic acid and heating the various mixtures in an oven for five hours. One series of reactions was carried out at a temperature of 100°C., another at 160°C.

At neither temperature did the first mixture react appreciably. The mixtures turned black considerably and solution was far from complete. In the case of the second mixture the reaction was somewhat better, although there was considerable decomposition, especially at 160°C. Very little excess stearic acid was found in these mixtures when they were subsequently extracted with ether. The third and fourth mixtures reacted with less decomposition ocurring, and there were correspondingly larger amounts of excess stearic acid found after the end of the reaction. There seemed to be little difference in the rate or completeness of the reactions at the two different temperatures. There was more decomposition at 160°C.

In view of the results of these tests, it was decided to try a series of reactions using equimolar amounts of lead glyceride and

stearic acid, since these were the proportions which should react completely and give the product predicted by theory. Therefore 4.215 grams of lead glyceride were mixed with 4.050 grams of stearic acid and the mixture heated in a crucible placed in an oil bath at 120°C. The mixture, when the acid had melted, was stirred with a small mechanical stirrer. In all of these reactions stirring increased considerably the ease with which the lead glyceride dissolved. After two hours of heating at 120°C. solution was complete. Some darkening of the mixture ocurred as the reaction progressed.

The reaction mixture was finely pulverized and refluxed with 100 c.c. of dry ether to remove any excess stearic acid. The amount of acid thus recovered was rather small, being about 0.8 gram. The product, after two extractions with ether, was filtered, washed and dried as before. The substance was a little darker in color than that originally prepared. The chemical properties of this substance were identical with those already stated for the substance as originally prepared, except that the melting point of the product was now 103°C.

One gram samples of the substance were analyzed for lead and the following results obtained.

	I	II
Weight of sample analyzed	0.9038 gms	1.2255 gms.
Weight of lead oxalate precipitate	0.4214 gms.	0.5731 gms.
Percentage of lead found	32.73 %	32.82 %
Average percentage of lead found		32.78 %

The percentage of lead in lead stearate is 26.78 % and in B-stearo-lead glyceride 36.77 %. In view of this fact, and in view of the properties of the substance prepared, it was thought that it was possibly

a mixture of the two above compounds. This possibility was not further investigated at the time.

Preparation of Tristearin.

Instead of further studying the B-stearo-lead glyceride, an attempt was made to prepare the same substance by the direct action of litharge on tristearin. Here the difficulty arose of obtaining tristearin in anything approximating a pure state. A survey of chemical literature revealed the fact that it is practically impossible to prepare this compoundpure from any natural source. In any event, it is an extremely laborious task, and one likely to yield uncertain results. Most naturally-ocurring fats contain mixed glycerides rather than simple triglycerides. Thus, Duffy[3], on recrystallizing 2000 grams of mutton tallow from large quantities of ether, obtained, after thirty-two successive crystallizations, no more than eight grams of substance, which even then could not be considered pure tristearin. Hence, for the preparation of pure triglycerides, synthetical methods are usually employed.

Pure triglycerides were first obtained by Berthelot[4], by heating glycerine with fatty acids. Monoglycerides and diglycerides were formed simultaneously. To prevent this, and to insure complete esterifi-

[3]Jour. Chem. Soc. 5, 199 (1852).

[4]Ann. de Chim. et de Phys., 3, 41, 420, (1854).

cation, Scheij[5] heated glycerine with an excess of fatty acid in a slow current of air. The reaction was considered complete when no more water was evolved. Pure triglycerides can also be prepared by heating together the sodium or silver salts of the fatty acids with tribromohydrin (Guth; Partheil and v. Velsen)[6].

More specifically, tristearin can be prepared by heating (a) monostearin with 15- 20 parts of stearic acid (Berthelot); (b) distearin with stearic acid (Guth); (c) glycerine with an excess of stearic acid (Scheij); (d) tribromohydrin with silver or sodium stearate (Partheil and v. Velsen; Guth). The original references to these methods of preparation were not available so that more detailed information concerning the methods of procedure could not be obtained. Lewkowitsch[7] mentions these methods but does not give any more detailed account of how to prepare tristearin. Nor could any reference be found in any available chemical literature.

An attempt was made to prepare tristearin by combining sodium stearate with trichlorohydrin, according to the equation

$$C_3H_5Cl_3 + 3\ C_{17}H_{35}COONa \longrightarrow C_3H_5(OOCC_{17}H_{35})_3 + 3NaCl.$$

Sodium stearate was prepared by adding 50 grams of stearic acid to a boiling solution of sodium carbonate containing twice the theoretical amount of sodium carbonate. After the stearic acid had

[5]Rec. d. trav. chim. Pays-Bas, 18, 169.

[6]Archiv d. Pharm. 238, 267 (1900).

[7]Lewkowitsch, Chemical Technology and the Analysis of Oils, Fats and Waxes; Vol. I, page 27.

entirely dissolved, ten grams of sodium hydroxide were added and the solution was boiled for half an hour to insure complete saponification. The sodium stearate was precipitated from the solution by saturating it with sodium chloride. The product was filtered off and dried in an oven for an hour at 100°C.

To 10 grams of sodium stearate was added the theoretical amount, 1.6 grams, of trichlorohydrin. The mixture was heated gradually to its fusion point, 275°C., in a crucible in an oil bath. The mixture fused with difficulty and considerable decomposition ocurred. The reaction mixture was kept at the above temperature for an hour, then cooled, pulverized, and extracted with hot benzene. The amount dissolved by this solvent was negligible, whereas tristearin is readily soluble in hot benzene. The desired reaction had evidently not taken place under the conditions used.

An attempt was next made to prepare tristearin by the reaction between glycerine and stearic acid, according to the equation

$$C_3H_5(OH)_3 + 3\,C_{17}H_{35}COOH \longrightarrow C_3H_5(OOCC_{17}H_{35})_3 + 3\,H_2O.$$

3.3 grams of ordinary 90 % glycerine were placed in a 250 c.c. distilling flask with twice the theoretical quantity, 55 grams, of stearic acid. The flask was connected to a condenser and heated on an oil bath to a temperature of 110°C. When the acid had melted, a slow current of air, dried by concentrated sulfuric acid, was passed through the reaction mixture by means of a capillary tube extending to the bottom of the distilling flask. The mixture was kept at a temperature of 100°- 110°C. for a period of seven hours. Water appeared on the neck and side tube of the flask and the two layers of liquid united to form a homogeneous mixture. At the end of seven hours no more water was evolved and the reaction was considered complete. The reaction mixture, after being pulverized, did not

resemble the original stearic acid in appearance. It had a slight yellow color and a melting point of 51°C. The original stearic acid used melted at 60°C. The reaction had evidently produced a new substance which was hoped to be tristearin.

The tristearin was separated by removing the excess stearic acid with alcohol. Stearic acid has a solubility of 2.5 grams per 100 c.c. of alcohol at 20°C., whereas tristearin is practically insoluble in cold alcohol. Therefore, repeated extractions with cold alcohol should remove all stearic acid present without dissolving much stearin.

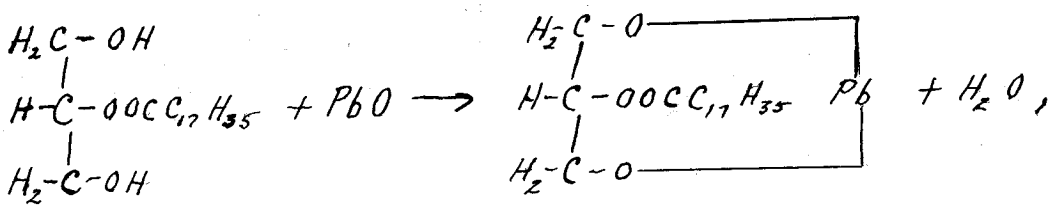
The pulverized reaction mixture was agitated for fifteen minutes with 250 c.c. of alcohol at 20°C. The undissolved matter was much whiter than the original mixture, most of the yellow color passing into the alcohol solution. The insoluble matter was separated by filtration. From the filtrate 14 grams of residue were obtained by evaporation of the solvent.

The insoluble residue was treated with 250 c.c. more of alcohol and refiltered. From this filtrate 8 grams of residue were recovered. The portion undissolved by the alcohol was again treated with 50 c.c. of alcohol and the residue filtered off. From this filtrate 4 grams of solid matter were recovered. A fourth extraction with 50 c.c. of alcohol produced very little substance soluble in the alcohol. It was therefore concluded that the separation had been made as far as possible.

The insoluble residue was now dissolved in the least possible amount of boiling alcohol and the stearin allowed to crystallize from the saturated solution. The crystals were filtered off from the cold solvent and recrystallized from ether. The final product was dried in an oven for an hour at 50°C. Seven and one-half grams of substance were so

obtained which was thought to be tristearin.

This crystallized substance melted at 67°C. If allowed to cool, it solidified at 63°C., melting thereafter constantly at 63.5°C. The product was less soluble in cold ether than stearic acid. It was only very slightly soluble in cold alcohol, but dissolved readily in benzene and chloroform in the cold. these properties correspond fairly closely with those given by Lewkowitsch[8] for tristearin, except that he gives its melting point as 71.6°C. The substance did not show, to any marked degree, the so-called double melting point characteristic of pure triglycerides. It was probably a mixture of tristearin with smaller amounts of mono- and distearin. However, the substance seemed to be as pure as it was possible to get it by the methods available. Furthermore, the presence of monostearin should not be especially objectionable in the reaction with litharge, since the two would probably react according to the equation



thus giving the same compound as that called for by theory for the litharge-tristearin reaction.

[8]Loc. cit.

Reaction of Litharge and Tristearin.

Equimolar amounts of litharge and the supposed tristearin were allowed to react in the following manner. Four grams of stearin were melted in a crucible heated in an oil bath. One gram of litharge was gradually added to the melted fat, the mixture being agitated with a mechanical stirrer. Very little reaction appeared to take place at a temperature of 110°C. The temperature of the bath was gradually raised to 160°C., when the substances appeared to react. The orange color of the litharge disappeared and the mixture darkened considerably. The presence of the litharge seemed to, in some manner, catalyze the decomposition, since stearin alone heated to this temperature showed no signs of decomposing.

The reaction mixture was kept at a temperature of 160°- 170°C. for two hours. The litharge entirely dissolved, forming a solution which was clear except for the presence of some carbon. One-half mole (0.5 gram) of litharge was added and allowed to react for one hour. This portion of litharge dissolved more slowly than the first portion, but it all finally went into solution.

The reaction mixture, after cooling, was pulverized and then extracted with two 50 c.c. portions of ether to remove any stearin or stearic acid present. The product was still somewhat dark in color, but was as pure as could be obtained by the methods used. As in the case of the product of the lead glyceride-stearic acid reaction, the substance would not dissolve completely in any solvent used, excepting turpentine. It was partially soluble in hot benzene and completely soluble in hot turpentine, but did not crystallize well from this solution.

The substance exhibited practically the same properties as the product of the lead glyceride-stearic acid reaction. It was hydrolyzed readily by boiling with acids or alkalies, with the formation of the corresponding lead salts and the separation of stearic acid. Its melting point, however, was 98°C., as compared with 103°C. for the supposedly same substance prepared by the lead glyceride-stearic acid reaction.

One gram samples of the substance were analyzed for lead, using the same procedure as before. The results were as follows:

	I	II
Weight of sample analyzed	0.6479 gms.	1.1440 gms.
Weight of lead oxalate precipitate	0.3274 gms.	0.5804 gms.
Percentage of lead found	35.47 %	35.61 %
Average percentage of lead found		35.53 %

These values corresponded more nearly with the theoretical value, assuming the substance to consist entirely of the B-stearo-lead glyceride. As before, this substance was probably a mixture of B-stearo-lead glyceride and lead stearate, the former being present in a somewhat larger proportion than in the previous case.

Lack of time prevented a further study of the substance prepared above. Aconsiderable amount of work was necessary to procure even a small amount of the product. The amount prepared was too small to use in making a separation of the product into its component parts, if any. The difficulty of obtaining tristearin readily and in a pure state seriously hampered the study of this third reaction. The results are not as conclusive and definite as they might have been, had an adequate amount of pure tristearin been available for use.

SUMMARY AND CONCLUSIONS.

The amount of work done on this problem wae somewhat limited by the time available during the year. However, it was thought that enough work had been done to make possible a fairly good analysie of the mechanism ofthe reactions involved.

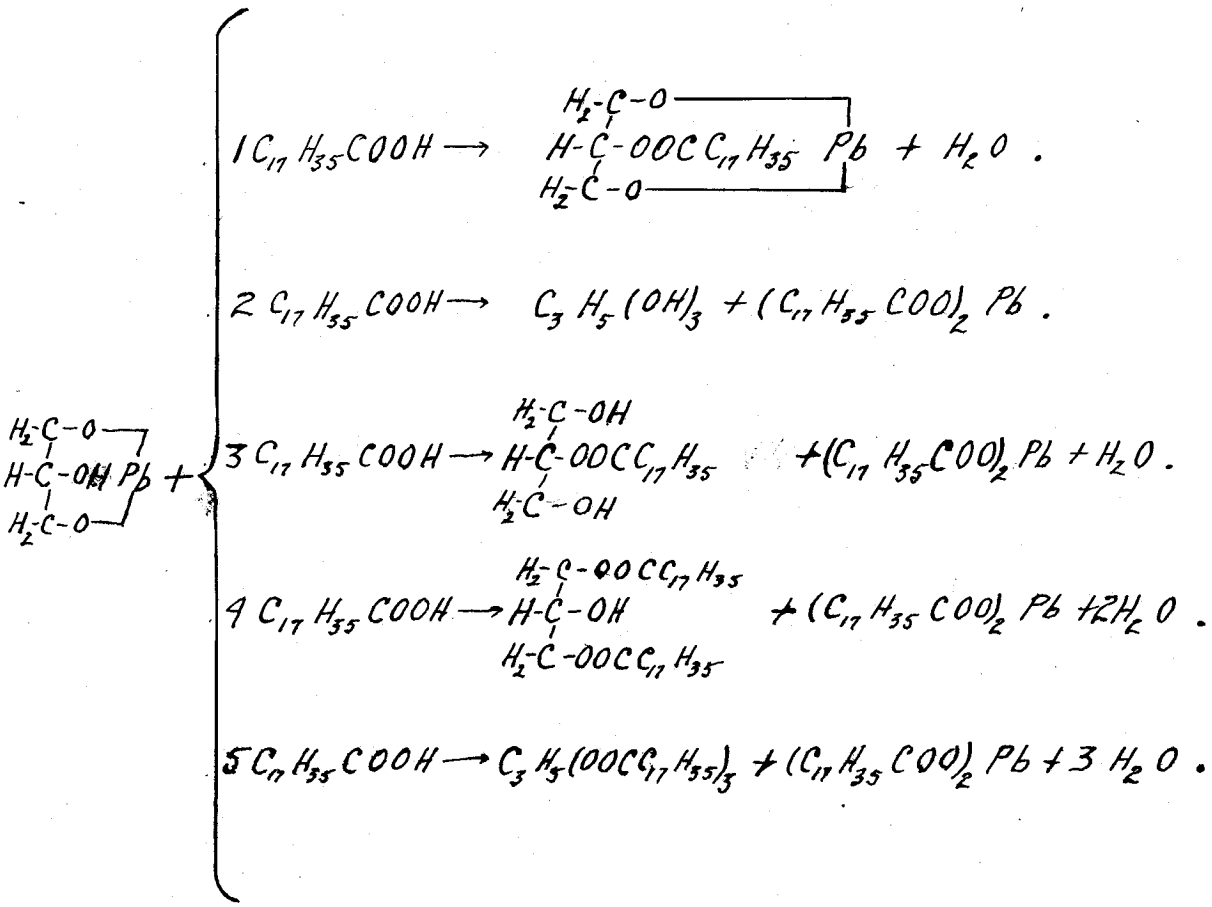
As already stated, the general method of procedure in this research was based largely on previoue work done on the same problem by Stoppel. Whereae he worked with linseed oil, this work was done using the simpler saturated glyceride, tristearin. The results should be similar, and, in the main, the propertiee and the compoeition of the compounde studied checked rather cloeely thoee given for the analegous compounds of litharge and lineeed oil. Discrepancies which did ocurr may have been due to a different behavior of the two glycerides, or, what is more likely, to differences in the methode of preparation and purities of the compounds.

The reaction between litharge and glycerine took place very easily and the resulting lead glyceride wae obtained in a practically pure state. No particular difficulty wae experienced in the preparation or analysis of this compound. The percentage of lead found checked the theoretical value within 1 %. Considering the fact that the compound could not be purified by the ueual method of recrystallization, due to its ineolubility in all solvente used, it was thought that this value was well within the limits of experimental error.

The reaction had evidently taken place as expected. The compound was a salt of lead and glycerine where two hydroxyl groups in the glycerine had been replaced by one atom of lead. As already explained, no

attempt was made to determine which two hydroxyl groups had been replaced, since this fact would be of no apparent importance in the ultimate analysis of the compound, nor in the reactions of the compound which were studied. It was sufficent to know that two, and only two, hydroxyl groups had been replaced by the lead. This fact was proved by the results of the analysis of the compound.

Having definitely established the composition of the lead glyceride, the next step was to determine how this compound reacted with stearic acid. Theoretically there are several possibilities. One molecule of lead glyceride could react with one, two, three, four or five molecules of stearic acid, according to the following equations:



It would be theoretically for any of these reactions to ocurr, either partially or completely. They might also ocurr independently or concurrently. The reaction mixture might therefore contain any or all of the following compounds: B-stearo-lead glyceride, lead stearate, glycerine, monostearin, distearin or tristearin.

It was thought that the first reaction was the one that would ocurr. It is the simplest reaction and the one predicted by theory. It was found that the lead glyceride would actually dissolve in the theoretical amount of stearic acid. However, the percentage of lead in the product was only 32.78 %, whereas B-stearo-lead glyceride should analyze 36.77 % lead. Errors in the work could hardly have produced so large a deviation. Therefore, it was concluded that the product contained some substance other than the above compound.

It can readily be shown that none of the other four reactions given above ocurred independently. For lead stearate, glycerine and the three glycerides of stearic acid are all soluble in hot benzene, whereas the actual reaction product would dissolve only partially in this solvent. The reaction product could hardly have contained any of the glycerides of stearic acid after purification, since these are all soluble in ether and would have been removed by the purification process. However, lead stearate is insoluble in ether, but soluble in hot benzene. Since the product was insoluble in ether and partially soluble in hot benzene, it was concluded that some lead stearate was probably present. This was the only possible reaction product, other than the B-stearo-lead glyceride, which could have exhibited the properties noted.

As already stated, the fractions of the product, separated by the treatment with hot benzene, were not quantatatively analyzed separately.

However, they were both compounds of lead, as evidenced by the fact that they both gave lead residues when ashed. About all that can be said here definitely is that they were probably lead stearate and B-stearo-lead glyceride.

The composition of the mixture varied with the conditions of the experiment. When an excess of stearic acid was used, a product containing 27.89 % lead was obtained. With equimolar amounts of lead glyceride and stearic acid, a product containing 32.78 % lead was obtained. Now lead stearate contains 26.78 % lead and B-stearo-lead glyceride contains 36.77 % lead. Hence it was concluded that an excess of stearic acid tends toward the formation of relatively larger proportions of lead stearate. In the first case above, the product must have been largely lead stearate. 32.78 % lead correeponds almost exactly to a mixture of two moles of B-stearo-lead glyceride and one mole of lead stearate. In any event, the product obtained in every experiment tried was a mixture rather than a single compound.

The third etep in the study of these reactions wae the direct combination of litharge and stearin. According to theory, it should be possible to dissolve two moles of litharge in one mole of stearin, according to the equation

$$C_3H_5(OOCC_{17}H_{35})_3 + 2PbO \longrightarrow \begin{matrix} H_2C-O \\ H-C-OOCC_{17}H_{35} \\ H_2C-O \end{matrix} \Big\rangle Pb + (C_{17}H_{35}COO)_2Pb .$$

Actually it was only found possible to keep one and one-half moles in

solution. An equimolar mixture of lead stearate and B-stearo-lead glyceride contains 30.98 % lead, whereas the actual reaction product analyzed contained 35.54 % lead. This latter fact indicated that it was largely B-stearo-lead glyceride. The reaction should have taken place according to the equation

$$2\ C_3H_5(OOCC_{17}H_{35})_3 + 3PbO + H_2O \rightarrow 2\ \begin{matrix} H_2C-O \\ | \\ H-C-OOCC_{17}H_{35} \\ | \\ H_2C-O \end{matrix} Pb +$$

$$(C_{17}H_{35}COO)_2Pb + 2\ C_{17}H_{35}COOH\ ,$$

assuming that only one and one-half moles of litharge could combine with one mole of stearin, and assuming that the fat used was wholly tristearin. The reaction product from this above reaction, consisting of two moles of B-stearo-lead glyceride per mole of lead stearate, should analyze 32.68 % lead. Actually, it analyzed 35.54 % lead. That it was actually impossible to keep more than one and one-half moles of litharge in solution was probably due to the fact that the fat used was not wholly tristearin, but contained some lower glycerides of stearic acid having fewer stearyl radicals per molecule. This condition evidently tended to the formation of smaller proportions of lead stearate in the product, there not being a sufficent number of stearyl groups to form both lead stearate and B-stearo-lead glyceride in the amounts called for by theory. In this case the formation of the B-stearo-lead glyceride seemed to take the preference. In other words, if the substance called tristearin had actually been pure tristearin, all available data and experimental evidence point to the fact that it would have been possible

to dissolve two moles of litharge in one mole of the stearin. The reaction would have taken place according to the equation given on page 24.

These conclusions are the best that could be drawn with the data at hand. There are so many possible reactions between litharge and stearin, and between lead glyceride and stearic acid, that it was impossible in the time available to thoroughly investigate all of them. The ones given are the most logical ones to expect, and, so far as could be determined, the ones which actually ocurr. As already stated, the difficulty of obtaining tristearin and the practical impossibility of determining the purity of the substance used as such added considerably to the uncertainty of some of the results obtained, and consequently to the interpretation of these results.

The deductions given can be applied by analogy to the litharge-linseed oil reaction. The results obtained in this research agree fairly closely with Stoppel's theory of the mechanism of these reactions. Enough work has been done to definitely establish the fact thatlead stearate, or lead linoleate, is not the sole product of the reaction, as has been heretofore supposed to be the case. It is probably not even the main reaction product. The formation of the fatty acid-lead glyceride seems to take preferance when only a limited amount of litharge is present.

Further work must be done on thie problem to definitely prove the theory given. A further study should be made of the separate reaction products with the view of determining the relative compositions of the mixtures produced when different proportions of the reactants are used. A further knowledge of the properties of the fatty acid-lead glyceride compound would probably be of some value and interest to the paint industry.